CONTAMINATED SITE INVESTIGATION USING NUCLEAR TECHNIQUE: A CASE STUDY OF TEMPORARY TRANSFORMER STORAGE SITES IN GHANA

THIS THESIS IS SUBMITTED TO THE DEPARTMENT OF NUCLEAR SCIENCES AND APPLICATIONS, UNIVERSITY OF GHANA,

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NUCLEAR AND ENVIRONMENTAL PROTECTION

By

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DECLARATION

This thesis is the result of research work undertaken by John Kudjoe Senu in the Department of Nuclear Sciences and Applications of the School of Nuclear and Allied Sciences, University of Ghana, Legon under the supervision of Dr. Joseph Richmond Fianko (SNAS) and Dr. Sam Adu-Kumi (EPA)

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DEDICATION

This work is dedicated to my families and my three children, Yayra, Etornam and Elikplim Senu for their support, inspiration and prayers throughout the period of this research work

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May the good Lord richly bless you and grant you all your heart desires

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LIST OF ABBREVIATION

ATSDR	Agency for Toxic Substance Disease Registry
BCMOE	British Columbia Ministry Of Environment
CCME	Canadian Council of Ministers of Environment
^{0}C	Degree Celsius
DDT	Dichlorodiphenyl trichloroethane
ECG	Electricity Company of Ghana Limited
ENAA	Epithermal
EOBr	Extractable Organobrominated
EOCI	Extractable Organo Chloronated
EOI	Extractable Organoiodinated
EPA	Environmental Protection Agency
EPRI	Electrical Power Research Institute
Fig.	Figure
FNAA	Fast Neutron Activation Analysis
GAEC	Ghana Atomic Energy Commission
GC	Gas Chromatography
GC-MS	Gas chromatography mass spectroscopy
GNIP	Ghana National Implementation Policy
H_2O_2	Hydrogen Peroxide
HPGe	High Purity Germanium Detector
INAA	Instrumental Neutron Activation Analysis

IUPAC	International Union of Pure and Applied Chemistry
LC	Liquid chromatography
µs/cm	microsiemens per centimetre
M	Molar
mg/kg	Miligram per Kilogram
mL	Millilitres
MNSR	Miniature Neutron Source Reactor
NCERC	Nuclear Chemistry and Environmental Research Centre
NEDco	Northern Electricity Distribution Company
NSAP	Nuclear Science and Application Programmes
PAH	Polycyclic aromatic hydrocarbon
PCB	Polychlorinated biphenyl
PCDD	Polychlorinated debenzo-p-deoxin
PCDF	Polychlorinated debenzo furan
PGNAA	prompt Gamma Neutron Activation Analysis
POPs	Persistent Organic Pollutants
ppb	part per billion
ppm	parts per million
PVC	Polyvinyl Chloride
RNAA	Radiochemical Neutron Activation Analysis
RPEC	Reverse Phase Extraction Chromatography
TSS	Temporary Storage Sites

UNEP	United Nation Environmental Programme
UNIDO	United Nations Industrial Development Organisation
USA	United States of America
USEPA	United States of America Environmental Protection Agency
VRA	Volta River Authority
XRF	X-ray fluorescence spectrometry

ABSTRACT

Recent introduction of man-made toxic chemicals, and the massive relocation of natural materials to different environmental compartments like soil, ground water and atmosphere, has resulted in severe pressure on the self-cleansing capacity of recipient ecosystems. Various accumulated pollutants and contaminants such as polychlorinated biphenyls (PCBs) are of much concern relative to both human and ecosystem exposure and potential health impact. PCBs which are resistant to degradation and bioremediation accumulate in different niches of the biosphere. This significantly affects ecological balance and cause adverse health effect on both human and the environment. Temporal transformer storage sites at four locations in Ghana (Tema, Tamale, Bolgatanga and Wa) were investigated for PCB contamination using nuclear techniques.

Analysis of soil samples from four temporal transformer storage sites revealed that the soil samples from Tema, Tamale, Bolgatanga and Wa were generally sandy with pH and EC ranging between 6.24 - 7.29 and 44.60 – 188.30 respectively. The PCB levels detected in the soil samples from the various locations varied considerably with mean ranging between 7.69 and 51.92 mg/Kg. The highest mean PCB level was recorded at the Tema temporal transformer storage site (51.92 mg/Kg), while the least mean level of 7.69 mg/Kg was recorded at Wa storage site. At Tamale the individual levels ranged between 3.57 mg/Kg and 38.70 mg/Kg while at Bolgatanga it was 6.85 – 16.30 mg/Kg and Wa, 6.08 – 14.70 mg/Kg. About 9% of soil samples from temporal transformer storage sites analysed had total PCBs concentrations above the 25 mg/Kg and 33 mg/Kg level recommended by the Canadian Council of Ministers of environment (CCME) and EPA Ghana respectively for the protection of environment and human health. Generally, the levels of PCBs in soil samples were found to decrease with increasing depth at all the temporal transformer storage sites.

Results obtained using the EPA's L2000DX PCB/ Chloride Analyser and Instrumental Neutron Activation Analysis (INAA) to analyse extractable organochlorine from the soil samples indicated that the nuclear technique is a better analytical technique for contaminated site investigation due to its high sensitivity, selectivity, fast and non-destructive nature. The INAA and gamma spectroscopy using HPGe detector coupled with MAESTRO 32 software provided a fast and efficient way to analyse possible PCB contamination in the soil samples and therefore proved to be very reliable method that could be conveniently used for contaminated site investigation

CHAPTER ONE

Introduction

1.1 Background

Advances in science and technology have enabled man to exploit natural resources to a great extent, generating unprecedented disturbances in global elemental cycles (Susarla *et al.*, 2002; Anyasi *et al.*, 2011). Recent introduction of man-made toxic chemicals, and the massive relocation of natural materials to different environmental compartments like soil, ground water, and atmosphere, has resulted in severe pressure on the self-cleansing capacity of recipient ecosystems. Various accumulated pollutants and contaminants are of much concern relative to both human and ecosystem exposure and potential impact. However, more efforts have been intensified by many countries to control the release of contaminants (Schnoor *et al.*, 1995; UNEP, 2005), and to accelerate the breakdown of existing contaminants by appropriate remediation techniques.

A contaminated site is an area of land in which the soil or underlying groundwater or sediment contains a hazardous substance in an amount that exceeds environmental quality standards (BCMOE, 1989; Ifeu, 1998). Contamination arises from obsolete stock of chemicals, manufacturing and formulation sites, waste disposal and incineration sites as well as leakage and spillage from point and non point sources.

Chemicals released into the environment may occur in a number of ways including disposal of solids or liquids in a landfill, undetected leaks or accidental spills, or non-point releases such as pesticide applications to agricultural land. Migration from a release will occur primarily downward into the subsurface. The velocity with which the contaminant spreads, the vertical and lateral extent of migration is largely dependent on the underlying site hydrogeology. Many sites in Ghana, for instance, became contaminated during past industrial or commercial activities

Chemical contaminants that are of national and global concern include those that have high persistence in the environment, high accumulative potential and high toxicity capabilities to human health. These include persistent organic pollutants (POPs) such as polychlorinated biphenyls (PCBs) which accumulate in different niches of the biosphere and significantly affect ecological balance (Graham and Ramsden, 2008). PCBs are also known to cause adverse health effect on both human and the environment (Fiedler *et al.*, 1998). These include disturbances in the liver, nausea, vomiting, jaundice, fatigue, alteration of lipid metabolism, hormonal changes and respiratory tract infection as well as a known carcinogen (IARC, 2004)

Polychlorinated biphenyls (PCBs) are world-wide environmental contaminants, resistant to degradation and bioremediation (Bedard *et al.*, 1987; UNEP, 2001). They are released into the environment through leaks from old and poorly maintained electrical transformers and the improper disposal of PCB-containing consumer products in municipal or other landfills not designed to handle hazardous waste. They are also released into the environment through their application in transformers and capacitors as dielectric fluid and heat transfer medium.

Although the use of PCBs and other POPs have been banned worldwide since 2000 (Nakata *et al.*, 2002), transformers that existed before then are still in existence. Some of these transformers are sited very close to densely populated residential areas, market places, hospitals and schools. Children and other individuals are likely to be affected when they are exposed to contaminants from these equipment in their vicinity.

1.2 Statement of the problem

The Electricity Company of Ghana (ECG) and the Volta River Authority (VRA) are directly responsible for capacitors and transformers for the production and supply of electricity in Ghana. They are the major custodians of PCB – containing equipment in Ghana and are responsible for their regular maintenance and services. Transformers and capacitors of ECG and VRA are always sited between two poles or on small concrete platform. These electrical gadgets contain oils that are stable at high temperatures and have excellent electrical insulating properties. During the filling, most of these oils drip or leak into the soil contaminating the whole area surrounding the equipment.

Available information from ECG and VRA indicates that Ghana officially ceased importing PCB – containing transformers and capacitors for use in Ghana since 1972 but evidence available to the Environmental Protection Agency in Ghana indicates otherwise (Yeboah *et al.*, 2005; GNIP, 2007). A preliminary assessment conducted by EPA-Ghana on transformers in the country revealed that out of 1000 transformer analysed 155 tested positive for PCBs, 33 of which were imported between 2004 – 2008 thus contradicting the claim by ECG and VRA that they have stopped the importation of PCB-containing transformers since 1972. Further evidence also indicates that some of the transformers in operation had been topped up with mineral oil over the years (Yeboah *et al.*, 2005). The poor handling of damaged electrical equipment, leakages, spillage during retro filling and illegal dumping of PCB-containing waste may cause adverse effect to human and the environment.

The importation and use of closed, semi-closed and open applications type of transformers and capacitors in Ghana are not properly monitored and documented. There is the possibility that the post –1972 transformers may also contain significant amounts of PCBs as a result of retrofilling with possible PCB-contaminated mineral oils (GNIP, 2007). The release of transformer oil containing PCBs into the environment is possibly being done out of ignorance about the adverse health impacts and effects on humans and the environment (Yeboah *et al*., 2005; Buah-Kwofie, 2008). Additional information gathered suggests that transformer oils are being taken secretly and sold to local entrepreneurs for manufacture of different types of hair creams and use it as lubricant for cutting tools, indicating that PCBs may be mishandled and mismanaged in our environment.

In spite of numerous transformers in Ghana, no comprehensive studies have been undertaken to evaluate the extent of contamination of PCB at transformer sites being used as temporary storage facility or as sites for installing transformers and capacitors. Ghana being a signatory to the Stockholm Convention on POPs is obliged to undertake research, development and monitoring of POPs including PCBs (UNEP, 2001).

1.3 Purpose and objectives

The purpose of the study is to investigate the extent of polychlorinated biphenyl (PCB) contamination of soils around temporary storage sites (TSS) and around transformer that tested positive for PCBs using nuclear analytical technique.

The specific objectives are to:

- Establish the presence of PCBs in soils at temporal storage site for transformers.
- To characterize the types of PCBs in the environment.
- Determine the Levels of PCBs in soil at different depths.
- To employ INAA as a potential analytical tool to validate results of the L2000DX PCB/Chlorine Analyser for monitoring soils, oils and other environmental matrices.

1.4 Justification

Site investigation is an important effect in the effectiveness of risk management of a contaminated site. The findings provide the basis for decisions on the need for, and type of, remedial action and, eventually, for the design and implementation of the necessary regulated actions. It collects enough data and knowledge to draw conclusions regarding the degree of contamination of the site, which might or might not pose significant risk. The final goal of contaminated site investigation is to assist in decision-making about which remediation techniques to apply to the site and with respect to the future use of the contaminated land. It also allows comparison of multiple sites on a risk-basis in order to decide on priorities for remediation. The site assessment also helps the regulator to identify potential risks associated with a particular site.

CHAPTER TWO

Literature Review

2.1 Persistent Organic Pollutants

Persistent organic pollutants (POPs), originating from a variety of human activities are toxic chemical compounds that resist natural chemical and biological breakdown in the environment. POPs can be conveyed for thousands of miles through air or water currents, and may be found in remote ecosystems far from their source, even in locations where POPs have never been used (WHO, 1993; UNEP, 2001). Through bioaccumulation, animals higher in the food chain and humans are more likely to have higher concentrations of these pollutants, often to the degree that they, as endocrine disruptors, may cause neurological and immune system disorders as well as malignancies. The Stockholm Convention, which intended to protect human health and the environment from the harmful impacts of POPs have identified twelve (12) chemicals including PCBs that are persistent in the environment (UNEP, 2001).

2.2 Polychlorinated biphenyls (PCBs)

Polychlorinated biphenyls (PCBs) are the chlorinated derivatives biphenyls and are manufactured by the direct chlorination of the biphenyl ring system (Sittig, *et al*., 1981; WHO, 1993). It is a dual-ring structure comprising two benzene rings which is linked by a single carbon-carbon bond. The nature of Benzene ring allows a single attachment of a chlorine substituent to each carbon atom; hence there are ten (10) possible positions for chlorine to replace hydrogen atoms in the original two benzene rings (Fig.2. 1).

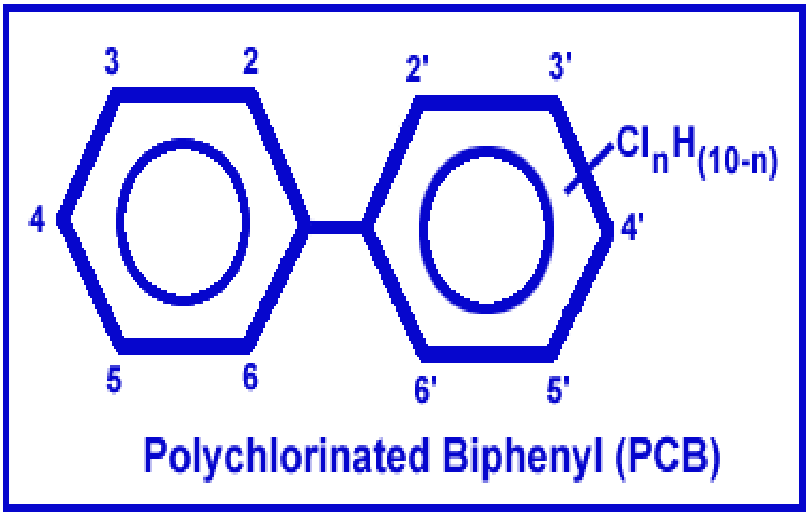


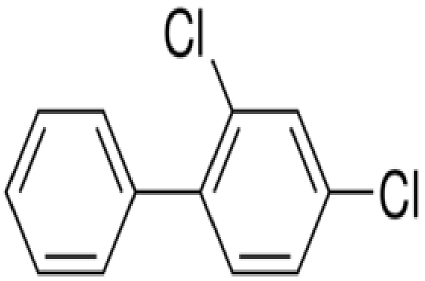
Fig. 2.1: Chemical structure of a PCB molecule

PCBs are soluble in organic solvents, oils and fats, but show an extremely low solubility in water especially the more highly chlorinated biphenyls. The arrangements of chlorine in PCBs have been shown to determine its toxicity, strength of adsorption to surfaces, and partition between various media. Although non-ortho, PCBs are often described as “the coplanar congeners,” 29 of which are of environmental concern as a result of their toxicity (UNEP, 1998).

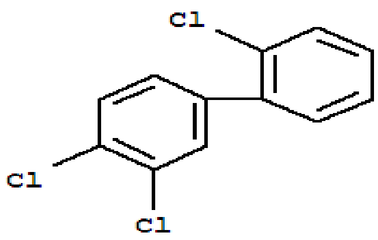
The solubility of PCBs is influenced by the environment as these compounds or preparations show a strong affinity for sediment and organic fractions. Sorption of PCBs on suspended and bottom sediment in an aqueous environment would result in lower concentrations of PCBs in water (USEPA, 2008). Sorption on the dissolved organic fraction, on the other hand, will probably enhance the concentration of PCBs in water (Kolar *et al.*, 2007). PCBs have been shown to adsorb relatively rapidly onto plastic and glass containers (Sawhney, 1986). Due to their low solubility's in water, PCBs are often associated with solid fraction like particulate matter, soil, sediments of the aquatic environments. The adsorption reactions of PCBs in aquatic and terrestrial systems play an important role in determining their fate and transport in the environment. In general, sorption of PCBs increases with the degree of chlorination, the surface and the organic carbon content of the sorbents (Weber *et al*., 1983; Moore *et al*., 1984; Anyasi, 2012). PCBs are chemically inert compounds and resistant to chemical degradation reactions in the environment. However, photochemical breakdown of PCBs has been noted by several investigators (Andersson *et al*., 2000)

2.3 PCBs Congeners

PCBs with different numbers of chlorine atoms are referred to as congeners. The name of a congener indicates the total number of chlorine and the position of each chlorine (Fig.2.2). For example, 4,4'-Dichlorobiphenyl is a congener that comprises the biphenyl structure with two chlorine atoms, one on each of the two carbons at position 4 which is also known as Para positions of the two rings (USEPA, 2007).

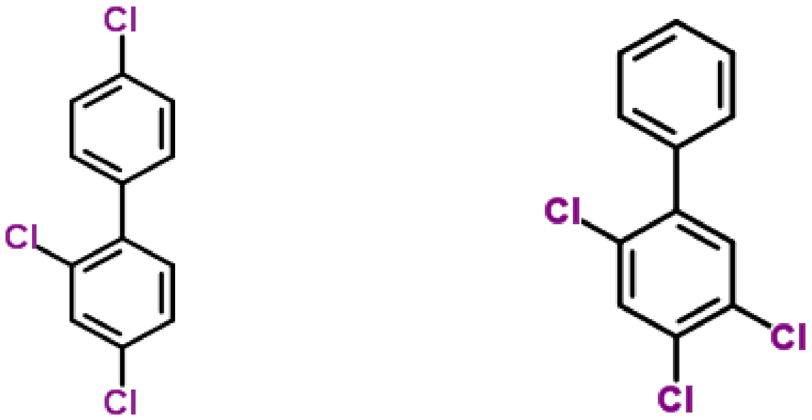


(a) 2, 4 – dichlorobiphenyl



(b) 2, 3, 4’-trichlorobiphenyl

(c) 3,3',4,4'-Tetrachlorobiphenyl (d) 4, 4′ -Dichlorobiphenyl



(e) 2,4,4'-trichlorobiphenyl (f) 2,4,5-trichlorobiphenyl

Fig. 2.2: Structures of some PCBs congeners

With the exception of Decachlorobiphenyl which has all its positions chlorinated, there is always more than one possible way to number the positions of the chlorine atoms. For example: 2, 3’, 4’-trichlorobiphenyl is the same as 2', 3, 4-tri... and is also the same as 2, 4’, 5’-tri.... this is because the two benzene rings are identical, and can rotate freely on the connecting bond (Clarke *et al*., 1989; Anyasi, 2011**).**

2.4 Uses of PCB

Generally, PCBs are thermally stable, excellent electrical insulators, sparingly soluble in water and have low flammability (Williams *et al*., 2001; Anyasi and Atagana, 2011). These characteristics make PCBs very useful in diverse industrial applications, such as liquid components of transformers, capacitors, heat-exchangers, and vacuum pumps. PCB mixtures have also been used in open systems like plasticizers, water-proofing agents, sealing liquids, fire retardants and pesticides (De Voogts and Brinkman, 1989). PCBs have also become a major component of varnishes, waxes, synthetic resins, epoxy, marine paints, and coatings, cutting oils, heat transfer fluids and hydraulic fluids. The non-inflammability of PCBs reduces the risk of explosion and fires in the event of a spark. They are therefore used as power transformers oils.

The uses of PCBs are in three main categories; closed partially closed and open systems. These classifications indicate how easy the PCBs contained within a product can escape to the surrounding environment.

A closed PCB application system is one in which the PCBs are held completely within the equipment. Under ordinary circumstances, no PCBs would be available for exposure to the user or the environment (WHO, 1993). However PCB emissions may occur during equipment servicing, repairing and decommissioning, or as a result of damaged equipment. It is estimated that 2 % of transformers and 3 % of large capacitors in the USA had leaked (Ifeu, 1998). Electrical transformers and capacitors (power factor capacitors in electrical distribution systems, lighting ballasts, motor start capacitors in refrigerators, heating systems, air conditioners, hair dryers, water well motor, capacitors in electronic equipment including television sets and microwave) are all in closed system category (Williams *et al*., 2001).

In the partially closed systems PCB containing oil is not directly exposed to the environment, but may be exposed periodically during the operation of the gadgets. Some of the applications in this category include; heat transfer fluids, hydraulic fluids, vacuum pumps, switches, voltage regulators, electrical cables and circuit breakers. Open systems applications involve PCB-containing items that are in direct contact with the general environment, some of the application in this category include. Plasticizers used in PVC, neoprene, and other chlorinated rubbers, lubricants, casting waxes, surface coatings, adhesives, inks, flame-retardants surface coatings.

2.5 Fate and Distribution of PCBs in the Environment

PCBs are ubiquitous environmental contaminants. It is estimated that about 400,000 tonnes of PCBs are present in the environment representing about 30% of the world's production (Buah-Kwofie, 2008; Anyasi and Atanaga, 2011). Of this total burden, approximately 60% is to be found in the hydrosphere; 1% in the atmosphere and the reminder in the terrestrial environment. Transfer of PCBs to the environment occurs through atmospheric deposition. Once deposited, the PCB tends to accumulate in soil for a long time. They are subject to various partitioning, degradation and transport processes depending on their physico–chemical properties. Approximately 98% of the PCBs entering the ocean are currently deposited from the atmosphere. Factors such as air temperature, wind speed, storm frequency, rainfall rates and the volatility of individual PCB isomers influence the pattern and rates of PCB movement in the atmosphere (Erickson, 1986; USEPA, 2008; Anyasi, 2012). The principal transport route for PCBs through aquatic systems is from waste streams into receiving waters, with further downstream movement occurring by solution and re-adsorption onto particles as well as by the movement of sediments. This situation makes marine environment one of the final sinks for PCBs.

PCBs are found in higher concentrations in the sediments of aquatic systems due to their chemical and physical properties which cause high sorption reactions. Sorption increases with chlorine content, surface area and the organic content of the sorbent. PCBs sorbs onto falling sediments that eventually ends up at the bottom sediments (Hoff *et al.*, 1994). PCBs are associated particularly with suspended sediments of a diameter less than 0.15 mm (Fernande *et al.*, 1997). The release of PCBs from sediments to overlying waters can occur by slow desorption, especially when PCB concentrations are high or when sudden hydrographic activity like flooding or dredging causes sediments to be re-suspended and redistributed. Translocation can also occur through biological activity (UNEPA, 1998).

The concentrations of PCBs in sediments depend upon the characteristics of the sediments and their proximity to the source. In the vicinity of waste outfalls, residues may range from 2 to 500 µg/g (EPA, 1983). Elevated levels of PCBs have been measured in sediments off certain industrial facilities for example up to 1.0 µg/g was measured in sediments adjacent to the Belkin Paperboard paper recycling plant in Burnaby (Wania *et al.*, 1996). In British Columbia, total PCB concentrations in freshwater sediments are generally below detection limits (BCMOE, 1989). However, the concentrations in marine sediments have been measured up to 16.8 µg/g off the

Bayshore Inn in Coal Harbour, 17 µg/g in the vicinity of Burrard Yarrow Shipyards in Burrard Inlet, 6.9 µg/g under the Granville Street Bridge in the False Creek area of Vancouver, and 3.6 µg/g in Victoria's Inner Harbour (Wania *et al.*, 1996).

Sorption reactions also affect transport of PCBs in soils. PCBs that are sorbed by soils, especially the highly chlorinated ones, remain significantly immobile against leaching (Erickson *et al.*, 1986). They are also unlikely to be taken up by plants and therefore are not readily mobile in soil systems. Vapour phase transport may allow for redistribution or migration through the saturated soil pores (Chow *et al.*, 1993). PCBs do not generally occur in soil environments, except when spills, industrial releases, atmospheric transport, or application of sewage occur. USEPA (1976) reported that agricultural soils in the U.S. rarely contain detectable levels of PCBs; although PCBs were frequently detected in soils from urban areas where there were many transformers and capacitor.

2.6. Environmental occurrences

PCBs are widespread contaminants in the environment primarily in soil and freshwater systems (Erickson, 1986). Their persistence in the environment has been a growing concern due to their low degradability, toxicity, mutagenicity and the tendency to bioaccumulate (Bedard and Habel, 1987). Before the 1980s polychlorinated biphenyls were widely used worldwide as coolants and insulators in electrical capacitors and transformers; and as plasticizers in paint and rubber sealants. Large quantities of PCBs have since entered the environment through leakage, disposal and evaporation (Gaofeng Zhao *et al.*, 2006). The predominance of PCB in the environment continued from its persistence and bioaccumulation in different matrices of the environment (air, topsoil, sediments, food, fish) (Eisenreich *et al.*, 1999; Anyasi, 2012). Majority of PCB in the air results from volatilization of PCBs from industries, leaking contaminated transformer oil, soil and water. Some PCBs were released to the atmosphere from uncontrolled landfills and from hazardous waste sites; incineration of PCB containing wastes; leakage from older electrical equipments in use and improper disposal and spills (Bremle and Larsson 1998; Buah-Kwofie, 2008; Anyasi, 2012).

PCBs are ubiquitous compounds and their levels generally increase from lower to higher tropic levels (Bright *et al.*, 1995; Willman *et al.*, 1997; Anyasi, 2012). PCBs released into the environment are partitioned between different media and transformed through a range of processes, such as photolysis, microbial activity, and metabolism. Among the 209 PCB congeners, 36 are environmentally threatening as a result of their environmental prevalence, relative abundance in animal tissues, and potential toxicity (McFarland and Clarke, 1989). According to Bignert (1998) the total PCB level in muscle of herring caught along the Swedish coast ranged between 510 and 2400ng/g lipid. In a sediment core from the North-western Baltic, the levels of PCBs peaked in the 1978 at 11 ng/g (dry weight) (Kjeller and Rappe, 1995; Anyasi and Atagana, 2011). A decreasing trend of PCB levels has also been observed in archived herbage samples (Jones *et al.*, 1992), peat and sediment cores (Sanders *et al.*, 1992, 1995), and stored air filter samples (Jones *et al.*, 1995).

While it is believed that the total amount of PCBs produced annually has declined since the 1970s, this does not necessarily imply that the toxicological threat posed by these compounds has also decreased (Howard *et al.*, 1991). In Germany, PCBs are being buried in the shafts of salt mines. In such disposal facilities, residues will eventually find their way to watercourses and to the sea (Phillips, 1994). This implies that ecotoxicological problems created by PCB contamination will be evident for many years to come, despite the restrictions on PCB utilization. The non-ortho coplanar PCBs which are very persistent in aquatic environments have been found to the isomers of greatest toxicological threat (Tanabe *et al*, 1991, 1994). Significant levels of these PCBs may therefore bioconcentrate in exposed organisms and it is also probable that such compounds are transferred through the food web (Phillips, 1994; Adu-kumi *et al.*, 2010). Air samples collected around the Baltic Sea indicated a median current concentration of total PCBs of 57 pg/m^3 and higher PCB levels (89-370 pg/m^3) in the air were found at sites near the Great Lakes (Agrell *et al.*, 1999; Eisenreich *et al.*, 1999). Atmospheric levels of PCBs are correlated with temperature, thus, higher concentrations of the highly chlorinated PCBs are found during the summer (Hileman, 1988; Haugen *et al.*, 1999).

There are five main sources of PCBs emission into the environment. These include production of PCBs and products (equipment) containing PCBs; use of products containing PCBs; utilization of PCBs and materials containing PCBs; emission from reservoirs polluted by PCBs and thermal processes. Another source or category includes contaminated soils, bottom sediments, waters that act as secondary sources of PCB emissions (Bremle and Larsson 1998; Jiamo Fu *et al.*, 2003). The European PCBs emission inventory for 1990 also enumerates the following as the sources: coal combustion, steel smelting (open-hearth, converter, electric), sintering, and waste incineration, electrical equipment (capacitors and transformers) (Berdowski *et al.*, 1997).

PCBs may also be transported for long distances by air, rivers and ocean currents and contaminate regions remote from their source (Borja *et al.*, 2005). Other sources of PCB emission include treatments, storage, disposal facilities and landfills; hazardous waste sites; steel and iron reclamation facilities like auto scrap burning as well as accidental release of PCB to the atmosphere (Borja *et al.*, 2005; Bentum *et al.*, 2012). Sediments at the bottom of a water body can act as a reservoir from which PCBs can be released in small amounts to water.

2.7 Toxicity of PCBs on Human

There are a number of health related effects associated with exposure of PCBs. These include effects on the immune system, the reproductive system, the neurological function and the endocrine system. The effect of PCBs on human health depends on the extent of exposure or the concentration and type of PCB, the toxicity of the exposed PCB, or whether the exposure occurred through the lungs,, mouth or skin contact. Exposure through the food chain is the most important route of human exposure to PCBs. Phytoplankton is the primary food source of all sea organisms and a major source of oxygen in the atmosphere. The transfer of PCBs up the food chain from phytoplankton to invertebrates, fish, and mammals can result in human exposure through consumption of PCB-containing food source (Tanabe, 1988). Work done by Mace *et al.* (1994) suggests that the potential cancer risk to human increases with increasing hydrophobicity of the PCB and this potential increases when food chain sources of PCBs are added.

There is strong evidence that PCBs are carcinogenic to animals and it is reasonably anticipated to be carcinogenic in human (IARC, 1978b; ATSDR, 2000; IARC, 2005).

PCB exposure is associated with cancers of the liver, intestine and biliary tract as well as skin melanoma (Kimbrough *et al.*, 1995). Symptoms that have been reported from exposure to PCB contaminated rice oil include hyper secretion and enlargement of the meibonian gland of the eye, swelling of the eyelids and pigmentation of the nails and mucous membranes (Camille *et al*., 1988; Buah-Kwofie, 2008). These were associated with fatigue, nausea and vomiting. These symptoms were followed by hyperkeratosis and acne-like eruptions, which were most often noticed around the neck and the upper part of the chest. PCBs 3, 4, 3, 4 – Tetrachlorobiphenyl and 2,3, 4, 7, 8 – pentachlorodibenzofuran have been linked to heavy and severe pigmentation of conjunctiva, abnormal cystic acneiform eruptions and follicular accentuation. Skin and nail pigmentation, swelling of the eyelids and increased discharge from the eyes, headache, nausea, and numbness of the limbs in humans (Camille *et al*., 1988; ATSDR, 1998; Anyasi, 2012)

In epidemiological studies the general health effects associated with exposure to PCBs include many systemic changes (respiratory, cardiovascular, gastrointestinal, haematological, musculoskeletal, hepatic, renal, endocrine, dermal, ocular), immunological, reproductive and developmental (ATSDR, 1998). Some PCBs can mimic or block the action of hormones from the thyroid gland and other endocrine glands (ATSDR, 1994). The major blood disorders were decreased haemoglobin concentration, erythrocyte conc., gamma-immunoglobin and increased white blood cell counts

The proper development of the nervous system is very vital and has a significant effect on the health of individuals throughout their lives. Studies in both newborn human and monkeys exposed to PCBs commonly found in breast milk showed persistent decrease in neurological development, including visual recognition, short term memory and learning (USEPA, 2007). The similarity of effects observed in both human and animals provide additional support for the neurobehavioral effects of PCBs.

The absorption of PCBs by human and animals is through the skin, lungs and the gastrointestinal tract. Once inside the body, PCBs are transported through the blood stream to liver and to various muscles and adipose tissue where they accumulate (ATSDR, 2000). Research has also shown that effects on health depend on age, sex, and areas of the body where PCBs are concentrated (ATSDR, 2000; Green Fact, 2006). Studies have shown that PCBs has anti-oestrogen properties that can inhibit calcium deposition during egg shell development, leading to insufficient strong shells and premature lost (Shuler *et al.*, 1997; Borja *et a*l., 2005). The anti-oestrogen effects of PCBs may also lead to adverse effects on male reproduction capabilities of birds and animal species (Borja *et a*l., 2005).

2.8 PCB, a banned Chemical under the Stockholm Convention

PCBs have long been recognised as organic contaminants that pose threat to the environment because of their toxicity, persistence and tendency to bioaccumulate in the bodies of animals, particularly at the top of the food chain (UNIDO, 2004). Although the use of PCBs has been reduced greatly since the 1970s it is recognised that those still remaining in existing equipment pose a continuing environmental threat.

The Stockholm Convention signed in May 23, 2001 became operational on May 17, 2004 (UNIDO). The convention requires that all the 160 countries who are signatories to this convention should try to reduce or eliminates the twelve (12) known persistent organic pollutants (POPs). The Governing Council of the United Nations Environmental Programme (UNEP) in its decision 18/32 of May 1995 requested for an international assessment of twelve (12) POPs which are polychlorinated biphenyls (PCBs), aldrin, chlordane, dieldrin, dioxins, dichlorodiphenyltrichloroethane (DDT) and endrin. The rest are furans, hexachlorobenzene, heptachlor, mirex and toxaphene. Between September 1998 and December 2000, the Stockholm Convention which Ghana is a signatory was adopted.

The main aim of the convention is to protect human health and the environment from exposure to these POPs which include PCBs. It also seeks among other things to eliminate these POPs from the environment by 2025. Out of these 12 chemicals that were initially listed in the Convention as Annex A, eight (8) of these chemicals are pesticides and fungicides that are commonly use in many developing countries under restriction e.g. DDT, dioxins, furans and PCBs. Even though PCBs are sometimes formed unintentionally from combustion of municipal and industrial waste, they can also be produced intentionally from chlorinated organic chemicals (Williams *et al.*, 2001).

The Annex “A” of the Stockholm Convention requires that parties must take measures to eliminate the production and use of the chemicals listed but specific exemptions for use or production apply only to parties that register for them. Information gathered from Articles 10 and 11 of the Stockholm Convention on POPs talks about disseminating information to the public, create awareness, educate, carry out research, development and monitoring of POPs among the general population, policy and decision makers (UNEP, 2001). Article six (6), section d (ii) of the same Convention requires that waste containing POPs be 'disposed off' in such a way that the persistent organic pollution content is destroyed or irreversibly transformed so that they do not exhibit the characteristics of POPs. Or otherwise be disposed off in an environmentally sound way when destruction or irreversible transformation does not represent the 'environmentally preferable option'.

2.9 Analytical Techniques for PCBs analysis

PCB is a well known persistent organic contaminant found in various environmental media. In the past decades a variety of methods have been developed for their analysis in environmental, biological and food samples. These include gas chromatography (GC), high performance liquid chromatography (HPLC), PCB immunoassay kits and ion specific analysis, thin layer chromatography (TLC), spectroscopic (UV–visible spectroscopy) and immunogenic methods enzyme-linked immunosorbent assay (ELISA) (Mace, 1994). The choice of a particular analytical technique depends on factors such as availability of the instrument, technical expertise of the analyst, the cost of analysis among others and in some circumstances the matrix.

2.9.1 Gas Chromatography (GC)

Currently GC coupled with different detectors such as flame ionization detector (FID), electron capture detector (ECD) and mass spectrometer (MS) has found wide application in PCB analysis. The GC-MS has been the tool of choice because it has good sensitivity, selectivity, specificity, a high degree of standardization, sample throughput, and instrument ruggedness. The GC-MS is usually run in the electron ionization-single ion monitoring (EI-SIMs) mode because there is a good compromise between selectivity and sensitivity. The advantages of GC-MS over other techniques is its minimal amount of sample use and the ability to screen for more than one analyte during one run even though derivatization of extracted compounds is required before analysis (Lynn *et al*., 2007).

Preceding the GC-MS analysis, the matrices are subjected to ultrasonic extraction and clean up by solid phase extraction (SPE). The ultrasonic extraction of atrazine from soil gives acceptable recoveries (>70%). According to Sun *et al.* (1998), sonication was better extraction technique than the Soxhlet extraction because it provided higher extraction efficiencies and it was more economical, easily operated and reproducible.

Many researchers have found the GC very useful and technique of choice in PCB analyses. Anyasi, (2012) used the GC-MS to analyse PCBs in soil in South Africa while Luthy *et al*. (1997); Lulek *et al*. (1998); Lynn *et al*. (2007); employed GC-MS in the analyses PCBs in various matrices. In the GC-MS, additional useful information such as the molecular weight of the sample can be obtained.

2.9.2 Liquid Chromatography (LC)

This is another technique that can be used to analyse PCBs (Waid *et al*., 1986). It becomes important because most compounds that are not volatile enough for GC can be analysed using LC. Liquid Chromatography can also be coupled to different types of detectors for further analysis (Harris, 1995). The disadvantage of this technique is that, the resulting elution profile shows poor separation of the congeners. Hence identification of possible sources of contamination becomes so difficult. The method is not sensitive enough compared with either GC/ECD or GC/HECD.

2.9.3 Dexsil L2000DX PCBs/Chloride Analyser

The basic principal of the L2000DX system is to measure the total organic chlorine content of a sample and equate that to an equivalent concentration of the target or expected analyte. The organic chlorine present is assumed to be derived from the target analyte, then an upper limit is established for the compound in question. (If other organic chlorines are present, in addition to the target analyte, they are counted as the target analyte.) To accomplish this, all of the organically bound chlorine is converted into inorganic chloride and the resulting chloride quantified. Extraneous sources of chloride contamination such as road salt or sea salt are not detected (Alvia Gaskill, 1994). Once the total chlorine content of the sample is known, a conversion factor is used to convert the chloride concentration into an equivalent concentration of the target analyte. If the contaminant is known, the resulting concentration estimates will accurately correlate with the actual concentration of the analyte in the sample as determined by L2000DX analysis in the lab. If the contaminant is unknown, a conservative or worst case conversion factor is chosen to provide an upper limit for the concentration of the target analyte in the sample.

There are three basic steps involved in the chemical analysis for total halogen by the L2000DX:

- Sample Preparation
- Conversion to Inorganic Chloride
- Quantification

The sample preparation step determines the type of chlorine detected, i.e., organic, inorganic, or total, and is matrix dependent. The sample preparation can be as simple as collecting a transformer oil sample, or can involve the extraction of a soil or water sample. In the case of a wipe sample, the surface is wiped and the wipe-gauze is extracted. The steps involved in the conversion to inorganic chloride reaction and the chloride quantification are the same for all matrices. The steps in the conversion to inorganic chloride involve the reaction of the sample with metallic sodium and the extraction of the resulting chloride into an aqueous buffer system. A chloride specific electrode is used to quantify the extracted chloride. Using stored conversion factors, the chloride value is then converted to an equivalent concentration of the analyte. Mark *et al*. (1991) used L2000DX PCB analyser to assess Wisconsin Power and Light Company to obtain accurate result and then define PCB contamination during site investigations

2.9.4 Clor-N-Oil Test Kits (for only mineral oil)

These test kits are manufactured by General Electric Company of United States of America under a contract from the EPRI. It was evaluated by the Utah Power and Light (Mills *et al.*, 1985) and is designed to give an indication of whether a mineral oil contains more than or less than 50 ppm of PCBs. The test kit is designed to measure the chlorine content of the oil only. It gives positive indication when the chlorine concentration is greater than 21 ppm. The 21 ppm is based on the chlorine content of the least halogenated Aroclor (1242). The implication is that 50 ppm of Aroclor 1242 will contain at least 21ppm chlorine (USEPA, 1996). Buah-Kwofie (2008) analysed transformer oils in Ghana using Clor-N-oil test kits.

2.9.5 Nuclear techniques for PCB analysis

Neutron activation analysis (NAA) and X-ray fluorescence spectrometry (XRF) are non destructive methods for chemical analysis of different media. The XRF is used for the analysis of solids and liquids using an x-ray beam. The USEPA Method 9075 had recommended and describes the use of XRF to analyse both new and used oils including transformer oils for PCBs. The applicable range of this methodology is from 200 µg/g to percentage levels (USEPA, 1994)

Neutron activation analysis (NAA) stands at the forefront of techniques for the quantitative multi-element analysis of major, minor, trace and rare elements. Due to the high sensitivity and accuracy that NAA offers, it is usually used as the referee method when new procedures are being developed (Glascock, 2003). Diandou Xu *et al.* 2011 used INAA to investigate polychlorinated biphenyls (PCBs) and organochlorine pesticides in rainwater in China and concluded that instrumental neutron activation analysis (INAA) is the most convenient, and quick and the only analytical method currently available for simultaneously determination of extractable organochloronated (EOCl), extractable organobrominated (EOBr) and extractable organoiodinated compounds (EOI) in one extract. Buah-Kwofie (2008) also confirmed INAA as a possible faster and efficient alternative analytical tool to screen transformer oils for PCBs.

2.9.6 Advantages of Neutron Activation Analysis

Activation analysis in general offers many advantages, including excellent sensitivity, multi-elemental analysis detected at the parts-per-billion (ppb) level and very fast (Friedlander *et al.*, 1981). There are many other techniques that offer comparable sensitivity, but activation analysis has other important benefits such as high selectivity and simultaneous multi-element detection capability (Ehmann *et al.*, 1991), arising from the fact that radionuclides decay with characteristic half-lives and γ-ray energies. Nuclides can generally be selectively determined on the basis of their unique γ-ray energies, so a single irradiation of a sample can often yield data for several elements at once. In the event of interferences due to overlapping photo peaks, the desired selectivity can usually be achieved with the proper choice of timing parameters. Consequently, the appropriate nuclides can be individually quantified without the need to physically isolate the elements under investigation.

Another advantage of NAA is that the analysis can be performed on both solid and liquid samples without any chemical additions, less sample manipulation and free from reagent and laboratory contamination and is non destructive. Many instrumental techniques require a liquid sample, to this end; most chemical procedures include a sample digestion as in reverse-phase extraction chromatography (RPEC) (Chung et al., 1988) or elution step, Typically elements are stripped from the column with acid or organic solvent prior to the quantification by AAS (Sarzanini *et al.*, 1987), AES (Sarzanini *et al.*, 1987), ICP-MS or visible spectrophotometer (Van der Sloot *et al.*, 1977). The elution step is disadvantageous in that it tends to lower the attainable concentration factor of the pre-concentration procedure and may not always be quantitative or reproducible.

2.10 Principles of Neutron Activation Analysis

Neutron Activation Analysis is among the most sensitive methods used to measure the concentration of trace amount of many elements in biological, environmental, medicinal geological, forensic, archaeological samples. The analysis is based on bombarding (irradiating) a sample with neutrons (produced in a nuclear reactor by fission reaction), resulting in the production of a radioactive isotope of the element of interest. The amount (concentration), of the product radioactive nuclide obtained is measured by analysing gamma rays emitted by the radioactive isotope produced. The basic nuclear reaction in neutron activation analysis is:

$$ {}^{A}_{Z}X + {}^{1}_{0}n \rightarrow {}^{A+1}_{Z}Y + {}^{0}_{0}\gamma, \text{ or} $$

$$ {}^{A}X\,(n, \gamma)\,{}^{A+1}Y $$

where, Y is the radioactive isotope; n is neutrons and X the parent nuclide (sample).

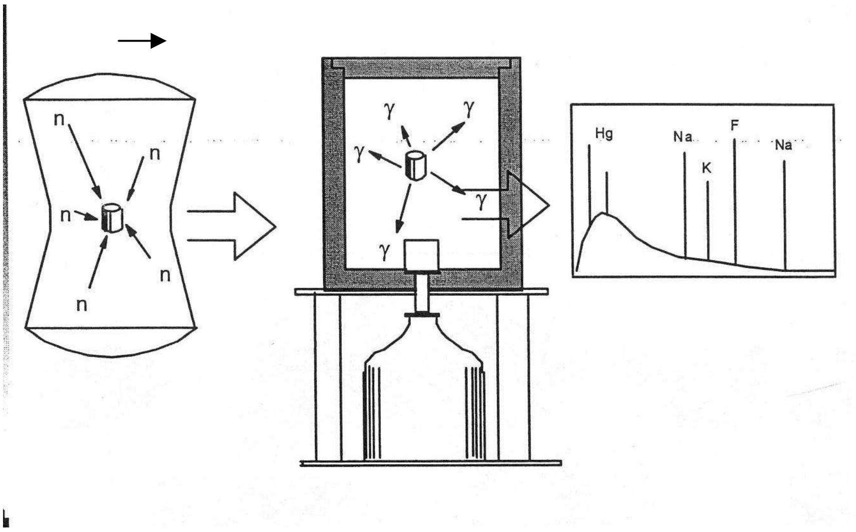
The irradiation times generally vary from few minutes to several hours depending on the half- lives of the elements of interest.

Table 2.1: Irradiation scheme for biological and environmental samples

Radionuclides	Irradiation time	Decay time	Counting time
Short-Lived	2 Minutes	I Minute	600 Secs
Medium-Lived	1 hr To 4 hrs	24-48 hr	600 Secs
Long-Lived	4 hrs	1-2 weeks	36000 Secs

After irradiation is terminated, the sample and standard are often allowed to decay (or “cool”). During cooling, short-lived interferences decay away so that they do not affect the outcome of the analysis. Another reason for allowing an irradiated sample to cool is to reduce the health hazard associated with counting the material. The decay time depends on the half-lives of the elements of interest.

Counting of samples is done on a High Purity Germanium Detector (HPGe) to obtain a spectrum on a PC-based gamma-ray spectroscopy system. The spectrum is then analysed qualitatively (for the elements present in the sample) and quantitatively (for the concentrations of the elements).The counting time depends on the half-lives of the elements of interest. The energy associated with the radiation emitted by the gamma rays is characteristic of the radioactive isotope, and hence it is used for element identification.



IRRADIATION COUNTING ANALYSIS

(REACTOR)

Fig. 2.3: Schematic diagram of INAA analysis processes

2.11 Quantification

The potential of employing nuclear reactions on samples followed by measurement of the induced radioactivity facilitates both qualitative and quantitative identification of the elements present in the sample. In general the technique involves the bombardment of a sample with radiation or particles. If the energy of the radiation or particle exceeds the threshold energy, a nuclear reaction will occur. Stable isotopes in the sample may be converted into radionuclides, which then undergo radioactive decay, a process accompanied by the emission of radiation. Detection of this radiation permits identification and determination of the elements present in the sample.

In order to quantify a particular element in a sample, it is necessary to relate the amount of that element to some measurable quantity (Guinn *et al.*, 1990). In neutron activation analysis (NAA), this quantity is the number of counts (C), taken as the number of γ-ray occurrences detected at a particular energy value. An irradiated sample is placed on a γ-detector and counted for a discrete period. The number of counts, C, registered during this counting period is given by the following equation:

$$C \quad = \quad (Nm/M)\, \sigma\phi\, O\text{€¥}\ )\ (1\ \text{-}e\ \text{-}^{xti})\ (e\text{-}^{xti})\ (1\text{-}e\text{-}^{xtc})$$

Where:

C	is the total number of counts registered,
N	is the Avogadro’s number,
m	is the mass of the elements (g),
M	is the atomic mass of this isotope.
σ	is the cross-section for the neutron capture reaction.
ϕ	is the neutron flux, to which the sample is exposed ($ncm^{-2}s^{-1}$),
O	is fractional abundance of the parent isotope,
€	is the detector efficiency,
¥	is the gamma branching ratio,

x is the decay constant of the nuclide (units of reciprocal time), and

ti, td, tc are the irradiation, decay and counting times.(Glascock, 2003)

2.12. Types of NAA

Among the various NAA methods instrumental neutron activation analysis (INAA) is the most common form of activation analysis and utilized for single and multi-elemental analysis. Instrumental indicates that no chemical treatment is performed on the sample for the irradiation process. The samples are packaged, irradiated for the specific length of time, allowed to decay, then counted and the element results evaluated and verified (Glascock, 2003)

Due to the problem of major element interference in INAA, a pre-concentration step may be inevitable. In pre-concentration NAA (PNAA) a cleaning process (chemical treatment) is carried out before irradiation, while in radiochemical NAA (RNAA) technique, the chemical treatment is done after the sample has been irradiated. Epithermal NAA (ENAA) is a process where neutrons of specific energy levels (from 0.1 to 1.0 eV) are utilized to suppress interfering agents from product radionuclide produced in high yields from undesired elements often with large thermal neutron cross sections. Prompt-gamma NAA (PGNAA) is based on the detection of prompt gamma - rays emitted from nuclei in an excited state during irradiation rather than afterwards. Fast NAA (FNAA) is based on reactions with high-energy (14 MeV) neutrons – produced by a specialized small accelerator (Guinn *et al*., 1990).

CHAPTER THREE

Materials and Methods

This chapter deals with the description of the study area, sampling techniques, sampling, samples, sample extraction, extract clean –up and PCB analysis. Chemicals and other auxiliary materials employed in this work were obtained from BD and Dexsil Corporate of United States of America, unless otherwise stated and were of analytical grade and used without purification.

3.1 Study area and Sampling site selection

The study was conducted at four temporary transformers stored sites (TSS). The sites are Tema in the Greater Accra Region, Tamale in the Northern Region, Bolgatanga in the Upper East Region and Wa in the Upper West Region of Ghana (Fig. 3.1). A field reconnaissance visits were undertaken to the entire study area to identify sampling locations. The choice of sampling sites was due to their strategic location, the bulk of temporal transformers stored in the area, transformer repair activities as well as population densities. Sampling was restricted to the transformer temporal storage sites

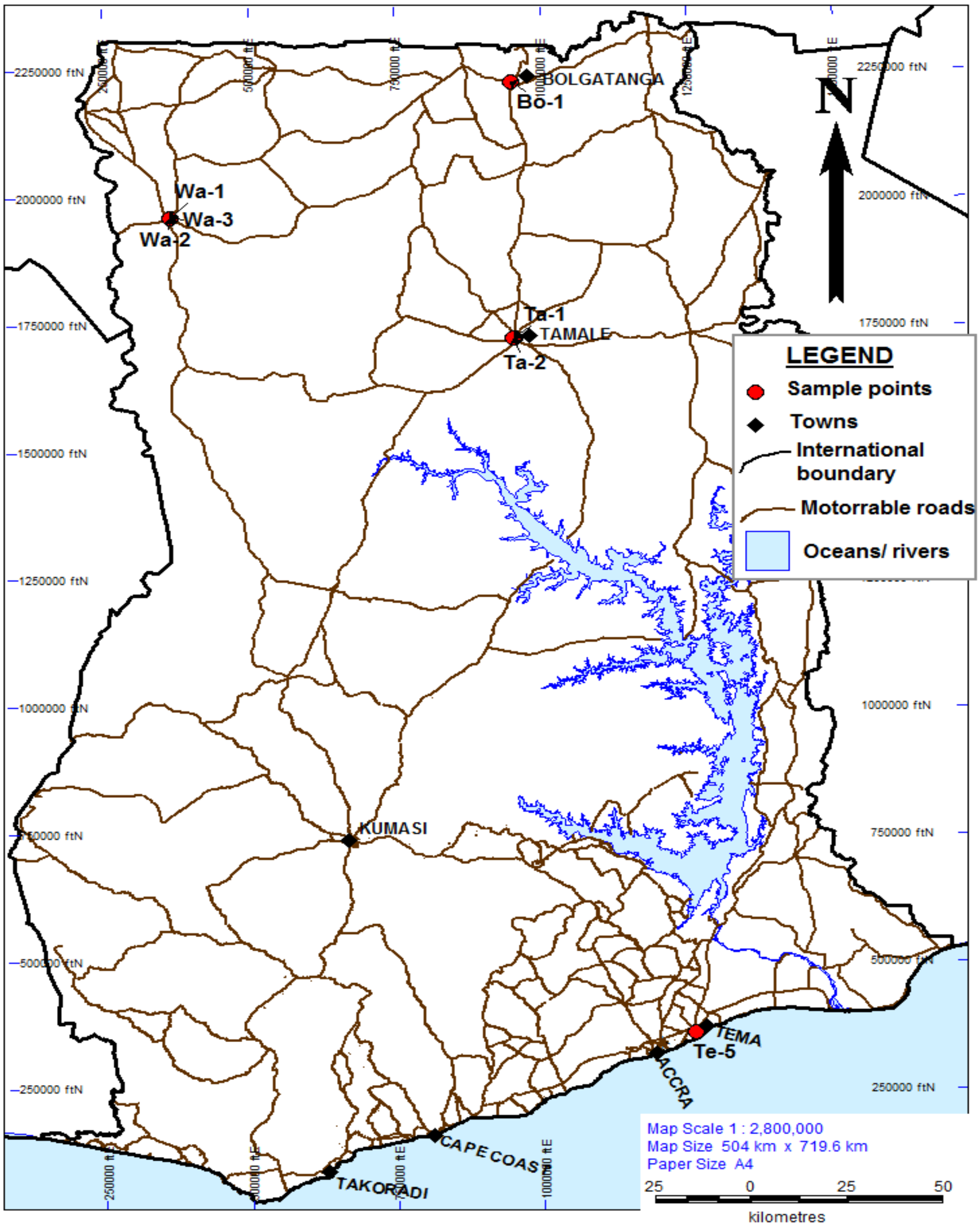


Fig. 3.1: Map of the study area showing sampling locations

3.2 Sampling

Soil samples were collected from the four temporary transformer storage sites in Tema, Tamale, Wa and Bolgatanga where transformers were kept and repaired (Fig. 3.2). The Temporary transformer Storage Sites in Tamale, Wa and Bolgatanga is being managed by the Northern Electricity Distribution Company (NEDCo) of the Volta River Authority (VRA) while that of Tema in the Greater Accra Region is managed by the Electricity Company of Ghana Limited. A total of sixty (60) soil samples were collected from different locations (Fig 3.1) in the four regions of Ghana from November, 2012 to March, 2013.

(a) Tema site

(b) Tamale site

(c) Bolgatanga site (d) Wa

Fig. 3.2: Temporal transformer storage sites at different locations

At each sampling site three (3) soil samples were collected with auger and a garden hand trowel, at depths of 0 - 10 cm, 10-20 cm and 20-30 cm as prescribed by Teng *et al.*, (2004). The soil samples were wrapped in clean aluminium foil and then bagged in polyethylene bags with hermetic seals (zip-lock bags). The samples were then transported to the Nuclear Chemistry and Environmental Research Centre (NCERC) laboratory of Ghana Atomic Energy Commission (GAEC) at Kwabenya for analysis..

3.3 Laboratory Analysis

At the laboratory, soil samples were disaggregated and air-dried in a clean room at room temperature for 3 days. The dried samples were screened through a well conditioned 250 µm mesh nylon sieve for two minutes to remove small stones and other materials which were not needed for the analysis. The samples were further screened in 125 µm mesh sieve to obtain smaller grain-sized sand particles and weighed.

3.4. Soil Characterisation

3.4.1 Particle size analysis

The hydrometer method was used in the determination of the percentage of sand, silt and clay. It involves the treatment of the sample with sodium hexametaphosphate. Prior to determination, the soil sample was pre-treat to remove carbonates, organic matter and iron, using a buffer solution and hydrogen peroxide (H_2O_2). The detailed experimental procedure is presented.

Approximately 20 g of homogenized soil sample was placed into a 1liter beaker; 100 ml acetate buffer (1 M) were added and heated on a water bath (100 ^{0}C) until it gave off no effervescence. About 25 ml of the buffer were then added to the mixture successively until effervescence reoccurred. The mixture was then centrifuged and decanted. About 250 ml of deionised water was then added to the residue, centrifuged and decanted. About 15 ml each of deionised water and 30% Hydrogen Peroxide were then added to residue in a beaker; covered with a watch glass and allowed to stand overnight. The beaker with the residues was placed in a water bath (80°C) and 5-10 ml H_2O_2 (30%) added successively until decomposition of organic matter was completed as supernatant became clear. Water was then added up to 300 ml and boiled on a hot plate for about an hour to remove any remaining H_2O_2. The sample was cooled, centrifuged and decanted. Approximately 300 ml of water were then added to disperse the soil residues. The suspension formed was quantitatively transferred into a 1liter polythene bottle, where 20 ml of a dispersing agent [4% Sodium hexametaphosphate, $Na_6(PO_3)_6$ and 1% soda solution] and 400 ml of water were added. It was shaken for 16 hours on a shaker at speed of about 30 revolutions per minute (rpm).

The suspension was passed through a 50 µm sieve which was placed in a funnel positioned above a 1 liter sedimentation cylinder with a stand and clamp. The filtrate was then topped up with water to the 1liter mark and this was used for the clay and silt fraction determination. The sand fraction which remained on the sieve was quantitatively washed into a porcelain dish, evaporated on the water bath and dried for at least an hour.

3.4.2 Determination of sand fraction

The dried sand was transferred into the top sieve of a stacked set of the following mesh sizes; 250 µm, 100 µm and 50 µm. It was sieved for 10 minutes on the sieving machine at amplitude of 7 and intervals of 4. Each of the sieves was then emptied into a weighing dish and accurately weighed.

3.4.3 Determination of sand, silt and clay

Silt, sand and clay fractions of the soil samples were determined using a hydrometer. The suspension obtained from the separation of fractions was allowed to equilibrate thermally and temperature recorded. The sedimentation cylinder was covered and shaken after which a drop of amyl alcohol was added. The hydrometer was carefully lowered into the suspension and its readings recorded. The hydrometer was removed, rinsed and wiped to dryness. The hydrometer was reinserted into the suspension and the readings recorded at the following time intervals: 5, 120 and 960 minutes. This was also repeated for a blank sample. During the analysis, a standard soil of known particle size content was analyzed with each batch of samples to check for instrument calibration and procedural accuracy.

Calculation of percentage silt, sand and clay content of the soil samples were as follows:

Calculation of percentage clay composition:

- % clay = corrected hydrometer reading at 6 hrs., 52 min. x 100/ WS

Calculation of percentage silt composition

- % silt = corrected hydrometer reading at 40 sec. x 100/WS - % clay

Calculation of percentage sand composition

- % sand = 100% - % silt - % clay

WS = weight of soil sample used

3.5 pH Determination

Soil samples (5 g) was weighed and 25 ml of solution deionised water were added to this was thoroughly mixed using a glass stirring rod and allowed to stand for 30 minutes. The soil slurry solution was stirred every 10 minutes during this period. The suspension was left for an hour for temperature stabilization, after which the pH and Electrical conductivity were determined using WTW pH meter model 523 and portable HACH conductivity meter, respectively. Before taking readings, all equipment were adequately calibrated. The pH meter was calibrated with pH 4.0, 7.0, 9.0 buffers while the conductivity meter was calibrated using 10 μScm-^{1}, 500 μScm^{-1} and 1288 μScm^{-1} standard KCl solutions. After calibrating, the electrode was rinsed again with deionised water, then dabbed lightly with tissues to remove any film formed on the electrode before immersion into the soil slurry solution (about 3- 5 cm deep) and the reading of various parameters mentioned were taken after the values of the sample stabilised (Jackson, 1989)

3.6 Analysis of Soil for PCBs using L2000DX PCB Analyser.

PCB test kit L2000DX PCB Analyser was manufactured by Dexsil Corporation, USA, and supplied by EPA - Ghana was used to determine the levels of PCBs in the soil samples. Each kit contains a plastic reaction tube with a colourless solution, black dispensing cap, a gray ampoule (top) and a blue-dot ampoule (tube 1); an empty test tube with white-cap (tube 2); extract solution; rinse solution; calibration solution; electrode filling solution; filter; scoops; 10 cc syringe; drying columns (foil packed) and a second reagent box (a black capped glass vial containing soil extraction solvent and 20 ml empty white capped glass vial)

3.6.1 Sample preparation for analysis for PCBs using L2000DX PCB Analyser.

Soil sample (10 g) was weighed into the empty white capped test tube and the entire extraction solvent in the glass vial added to it. The mixture was capped tightly, shaken vigorously for 1 minute and allowed to stand upright for 2 minutes. The end of the blue drying column was attached to the tip of the syringe and tight fit. The black dispensing cap from the plastic test tube that contains two glass ampoules was removed, the syringe-drying column slided into the test tube which contains the two ampoules and the set up left to stand upright. The extraction solvent on top of the soil was removed and dispensed into the top of the open syringe barrel using the polyethylene pipettor. Fig.3.3 (i-xi) depicts some of the processes involved in soil sample preparations and analysis.

After 7 ml of solvent has been dispensed into the syringe, the plunger was replaced into the back of the syringe and pressure applied. The solvent then percolated through the drying column at the rate of 2 or 3 drops per second until 5 ml of the dry extract was recovered. The bottom of the (colourless) ampoule in the test tube and the top (gray) ampoule were each broken by squeezing the sides of the tube and shaken 10 seconds. It was then allowed to react for 50 seconds while shaken intermittently several times. Using the pipettor, 5 ml of extract solution were added to the black-capped tube, capped securely and shaken vigorously until the foam and dark colour disappeared. This was repeated with intermittent venting for 20 seconds and allowed to stand upside-down on the flat top of the cap for two minutes.

A polyethylene filter funnel was placed in one of the 20 ml glass vials and the black-capped test tube positioned directly over the top of the funnel and the dispenser nozzle opened. The organic phase which contained the extracted PCBs and extraxtable organochlorines (EOCl) was then collected and allowed to cool for 5 minutes (Dindal *et al.*, 2000).

(i) (ii) (iii)

(iv) (v) (vi)

(vii) (viii) (ix

Fig. 3.3: some of the processes involved in soil sample preparation and analysis

(i).white capped test tube with soil sample and extraction solvent **(ii)** extraction solvent being taken from top of soil **(iii) & (iv)** the mixture is beinf filtered through syringe drying column **(v)** Black capped test tube containing filtrate, blue and gray dot ampoules in diglme (*) Diglyme = 1-mehoxy-2-(2-methoxyethoxy) ethane **(vi)** gray ampoules was broken and mixure shaken **(vii)** Extraction solution was added and black capped test tube overturned for phase separation(viii) extractable organic phase was filtered into glass vial **(ix)** L2000DX being used to determined PCB and extractable organochlorines (EOCl).

3.6.2 Sample analysis

The steps required for using L2000DX for analysis is to check the performance of the electrode and the optima operating temperature. These were done by filling, draining and filling the electrode with Orion electrode filling solution which was connected to the BNC at the back of the L2000DX PCB analyser. The electrode was then placed in Rinse solution and swirled gently for output of current and temperature updated in millivolts (mV) and degree Celsius (^{0}C). For optimum performance of the electrode, the output voltage should read 140 mV or greater within one minute. If the electrode output does not reach at least 140 mV within the one minute, the Rinse solution was emptied and refilled till the required millivolts was obtained.

The system uses a single point calibration in the quantification process using 50 ppm chloride calibration standard. The calibration was repeated for every 20 measurements made or when there was a change in temperature ±5 ^{o}C within one hour. The electrode was neatly wiped and placed in each sample extract and its reading for PCBs and EOCl recorded (mg/kg).

3.7 Determination of extractable organic chloride using Instrumental Neutron Activation Analysis

The method involves preparation of sample, irradiation of samples, measurement of γ-radiation intensity, evaluation of γ-ray spectrum and calculation of concentration.

3.7.1 Sample preparation

About 200 mg of both extracted soil solution and L2000DX PCB/chloride standard reference material (Dexsil Corporation Hamden- USA) were pipetted into separate 5 ml sample irradiation capsule using an Eppendorf micro-pipette. To each of the capsules were added sucrose and cotton wool to solidify and prevent any possible leakages of the sample. The capsules were heat-sealed with an ERSAMS 600 soldering machine. The 5 ml sealed capsules were placed into a bigger polyethylene capsule (12 ml) stocked with cotton wool and heat sealed for irradiation.

3.7.2 Irradiation of samples:

The irradiation of the extracted solutions and standards were performed in Ghana's pool-in-tank 30 kW miniature neutron source reactor (MNSR) at a neutron flux of 5×10^{11} neutrons/cm^2 s. Samples and standards were transferred into the reactor by means of the pneumatic sample transfer system (at a pressure of 60 atm). Thus ^{37}Cl(n, γ)^{38}Cl. Chlorine-38 (Cl-38) is a short-lived radionuclide ($t_{½}$ = 37.3 min); therefore samples were irradiated for 120 seconds. At the end of each irradiation, the samples were returned from the reactor, allowed to 'cool' (decay) until the level of activities was within the acceptable limit for handling. This was followed by measurement of γ-ray intensity of ^{38}Cl.

3.7.3 γ-ray intensity measurement

The γ-ray intensity of the induced radionuclide ^{38}Cl in both sample and standard were performed on a Canberra high purity germanium (HPGe) semi-conductor γ-ray detector. Measurement time was 600 seconds. The detector was coupled to an ACCUSPEC multi-channel analyzer (MCA) via electronic modules. The detector has an efficiency of 25% and a resolution of 1.8 keV at the 1332.5 keV γ-lines of ^{60}Co. 'Cooling' time was chosen such that the dead time of the detector was less than 10%.

The ORTEC MAESTRO-32 γ-ray spectroscopy software was used for γ-spectrum acquisition. A plexi-glass source support was mounted on the detector during measurement of γ-radiation intensity in order to ensure easy and reproducible source positioning (De Corte, 1987). The γ-radiation intensity of samples were measured first, followed by standards.

3.7.4 Evaluation of γ-ray spectrum and calculation of concentration

The net peak areas of the acquired γ-spectra for samples and standards were evaluated at the two γ-ray energies of ^{38}Cl (1642 and 2167 keV) using the HPGe semi-conductor γ-ray spectrum evaluation software, ORTEC MAESTRO-32.

After accumulation of the spectra (sample and standard), their respective net peak areas were evaluated. By comparing the net peak area of sample with that of the standard, the concentrations of the analyte (Cl) was evaluated based on the relative standardization method of neutron activation analysis (NAA), through the equation

$$C_{As\_sam} = \frac{A_{sam} \cdot M_{std} \cdot C_{As\_std}}{A_{std} \cdot M_{sam}}$$

Where:

$$A_{sam} = \left(\frac{N_p}{t_m \cdot D \cdot C_m}\right)_{sam};$$

$$A_{std} = \left(\frac{N_p}{t_m \cdot D \cdot C_m}\right)_{std};$$

- A_{sam} and A_{std} are the activities of the sample and standard, respectively;

- N_P = the net γ-photo peak area;
- N_P = net peak area of radioisotope produced at a specific γ-energy line;
- $D = e^{-\lambda t_d}$ is decay factor (i.e. Correction factor for decay between start of measurement of sample and start of measurement of standard);
- $C_m = \frac{1-e^{-\lambda t_m}}{\lambda t_m}$ = measurement factor (that is correction factor for decay during the measurement);
- t_m = measuring time (sec.);
- λ = the decay constant; $\lambda = \frac{\ln 2}{T_{1/2}}$; $T_{1/2}$ is the half-life;
- t_d = the decay time between measurements of sample and standard (sec.);
- M_{std} = the mass of the standard used for analysis (g);
- M_{sam} = the mass of the sample used for the analysis (g);
- $C_{analyte\_std}$ = the concentration of the analyte in the standard (μg g^{-1}); and,
- $C_{analyte\_sam}$ = the concentration of the analyte being determined (μg g^{-1}).

CHAPTER FOUR

Results and Discussion

The results of the field survey and laboratory analysis are presented for discussion in the form of Tables and Figures in this section. Detailed results are at the Appendix.

4.1 Quality Control samples/Certified reference materials

The analytical results obtained using instrumental neutron activation analysis at the Ghana Atomic Energy Commission (GAEC) laboratory for the reference materials compared favourably with the recommended values (Table 4.1).

Table 4.1: Analytical results of Standard Reference Material, showing local laboratory results and recommended values

Element	Measured values	Recommended values
	NAA	
Cl-38	5.00	5.00
	11.47	10.00
	14.32	15.00
	21.08	20.00
	50.85	50.00
	L2000DX	
Cl-38	48.78	50.00
	49.65	50.00

4.2 Soil Characteristics

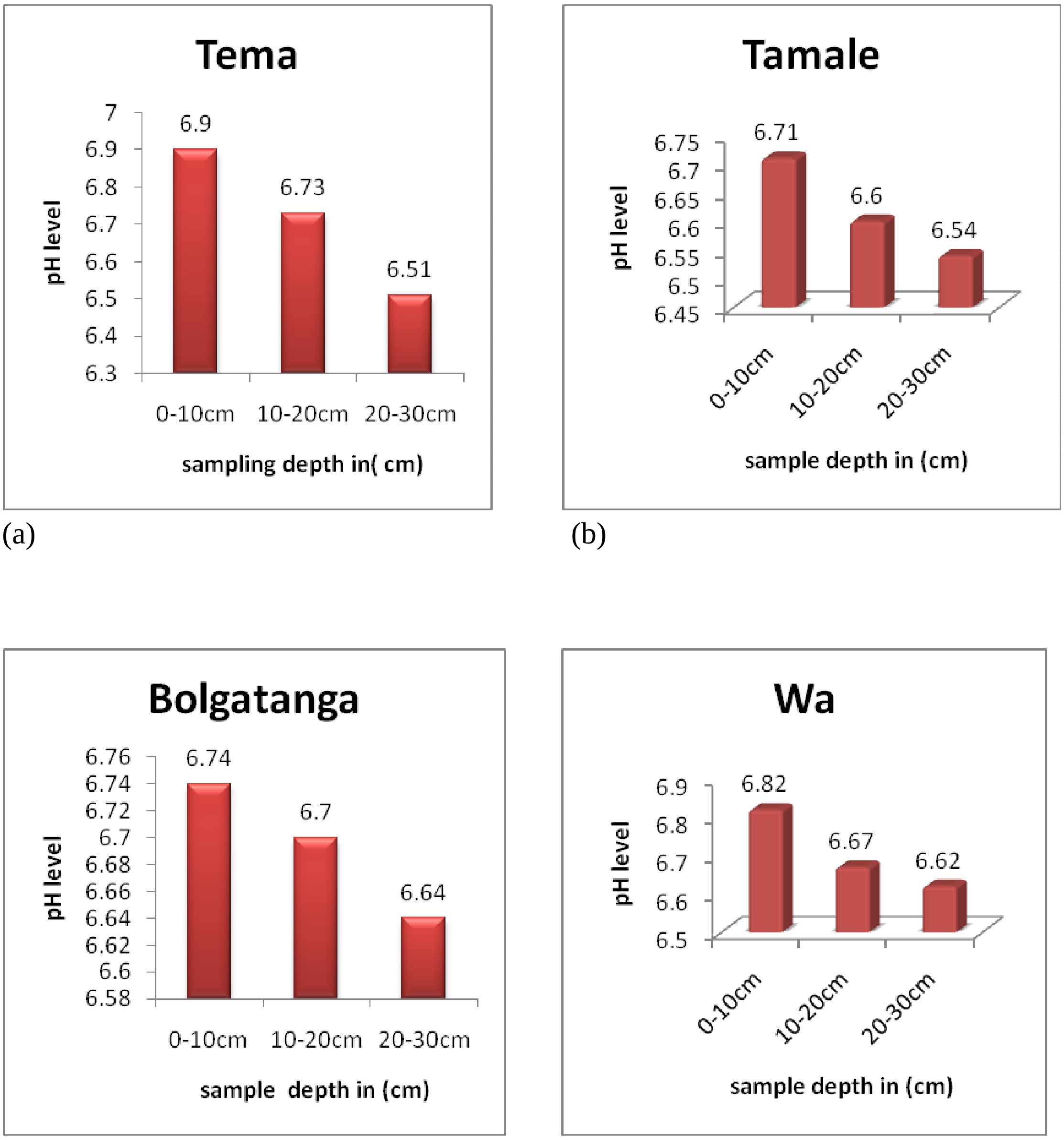
The characteristics of soil samples from the study area did not show any significant difference from one another. Generally, the study area had a sandy soil with Tema having about 85 % sand, Tamale 78 %, Bolgatanga 66 % and Wa 89 % sand. Clay and silt content of the soil samples were minimal. Apart from Bolgatanga and Tamale all the others had clay content of less than 15 % (Table 4.2).

Table 4.2: Characteristics of soil samples

Location	Soil composition (%wt)			Soil texture
	Sand	silt	clay	
Tema (Te)	85.07	4.91	10.02	loamy sandy
Tamale (Ta)	76.52	5.40	18.08	sandy loam
Bolgatanga (Bo)	66.03	16.02	17.91	sandy loam
Wa (wa)	88.89	1.13	9.98	sand

4.3 pH of soil

Soil samples from all the sample locations were slightly acidic. pH levels in Tema ranged between 6.24 and 7.29, while at Tamale the values recorded were 6.33 – 6.79, Bolgatanga 6.44 – 6.89 and Wa 6.41 – 7.05 (Appendix 1). There was an interesting trend observed in the analysis of the pH data. The pH in all the sampling points decreased with increased depth (Fig. 1 a – d). The increasing acidity with increasing depth could be attributed to decomposition of organic matter and other particulate matters in the soil by bacterial action which produced proton (H+) during respiration. Oxidation or reduction of hydrogen and hydroxyl ions may cause increase or decrease in pH value. According Ye *et al.* (1992) during anaerobic reductive dechlorination, highly chlorinated PCBs congeners in the soils are transformed to less chlorinate by replacing chlorine in biphenyl with hydrogen atom; this could also contribute to the high pH values at the top soil.



(a) (b)

(c) (d)

Fig. 4.1: Mean variation of pH level with soil depths

Geology (characteristics of the soil sampled) as well as residence time of dissolved ions as they migrate could contribute to gradual increasing acidity with respect to depth. Stranded migrating particulate matters and ions could also affect the trend exhibited by pH of the soil samples. Complexity of the soil matrices due to its heterogeneity might also affect the soil pH. At the Tamale TSS other items like car parts, used electrical gadgets were also kept in the same yard. Waste oil, battery water and rust metal could also leach into the soil thereby affecting the acidity. The characteristics of the soils sampled might speed up percolation of ions and chemicals which might have contributed to general and gradual decrease in pH values with increasing acidity with respect to depth.

4.4 Electrical Conductivity

Appendix 2 shows EC level of soil samples taken from four TSS in Ghana. The electrical conductivity (EC) levels of the analysed soil samples varied considerably. The EC in soil samples from Tema ranged between 44.60 and 151.40 µS/cm, Tamale 155.7 – 177. 30 µS/cm; Bolgatanga 72.60 - 188.30 µS/cm and Wa between 102.60 to 176.80 µS/cm. Electrical conductivity levels at Tamale and Wa were higher than the levels registered in Tema and Bolgatanga (Fig. 4.2). The variation in conductivity of the soil samples may be attributed to the geology and weathering of rocks in the sample location, deposition and decomposition of ions from mineral oils, industrial, municipal and domestic wastes. Even though the differences in the mean electrical conductivity (EC) levels detected at Tamale and Wa were significant the individual levels detected had no effect on the PCBs concentration in all the four transformer storage sites

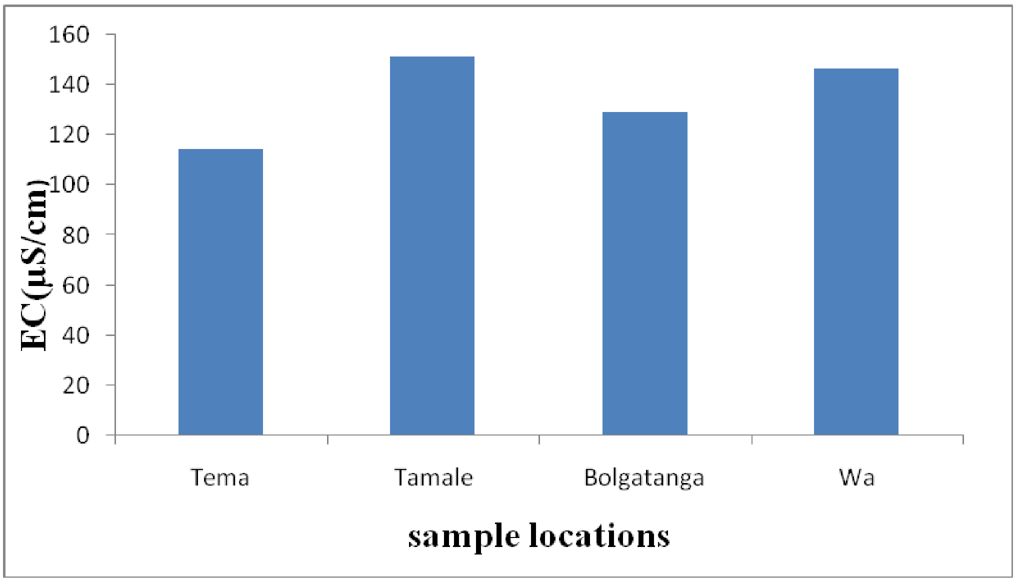


Fig. 4.2: Mean electrical conductivity of soil samples.

4.5 Variation of PCBs levels in soil samples from different locations

The study revealed the presence of PCBs in all soil samples analysed from temporal transformer storage sites at Tema, Tamale, Bolgatanga and Wa. The levels and the spatial distribution of total PCBs (Aroclor 1242) determined in soil samples from the different sample locations are presented in Appendix 6. The PCBs levels detected in the soil samples from the various locations varied considerably with mean ranging between 7.69 and 51.92 mg/kg (Fig. 4.3). The highest mean PCB level was recorded at the Tema temporal transformer storage site (51.92 mg/Kg) while the least level of 7.69 mg/Kg was recorded at Wa storage site.

The Temporal transformer storage site at Tema was the oldest among the four storage sites and housed most of the old and obsolete transformers that were brought into the country. Very few and newer transformers were found at the other three locations. The Tema yard also serves as storage site for decommissioned transformers and a training school for the Electricity Company of Ghana (ECG). Spillage and leakage from stored or damaged equipment, runoffs from other anthropogenic sources may contribute to the high PCB levels recorded at Tema storage site. Levels recorded at Tema were between 6.09 mg/kg and 518 mg/kg with sampling point Te-2 closer to a container housing pure PCBs - containing capacitors and other obsolete transformers. Tema is being the most industrialised community in Ghana and a harbour city; most of the industrial and municipal activities such as burning and improper disposal of refuse containing old electrical and electronic gadgets. Varnishes, waxes, synthetic resins, epoxy, marine paints, coatings, cutting oils, heat transfer fluids and hydraulic fluids, plasticizers used in PVC, neoprene and other chlorinated rubbers, lubricants, casting waxes, surface coatings, adhesives, inks, flame-retardants. Surface coatings may all contribute to the elevated levels of PCBs recorded.

Although the differences in the mean concentrations detected at Tamale, Bolgatanga and Wa were not significant, the individual levels detected varied significantly ($p<0.05$). At Tamale the individual levels ranged between 3.57 and 38.70 mg/kg while at Bolgatanga the range was 6.85 – 16.30 mg/kg and Wa, 6.08 – 14.70 mg/kg. Bolgatanga, Wa and Tamale are located in the Northern part of Ghana where temperatures are normally high; exposure of PCBs at the surface of soil to high temperatures might lead to evaporation since PCBs are volatile hence the climate might have contribute to the low level of PCBs at these locations.

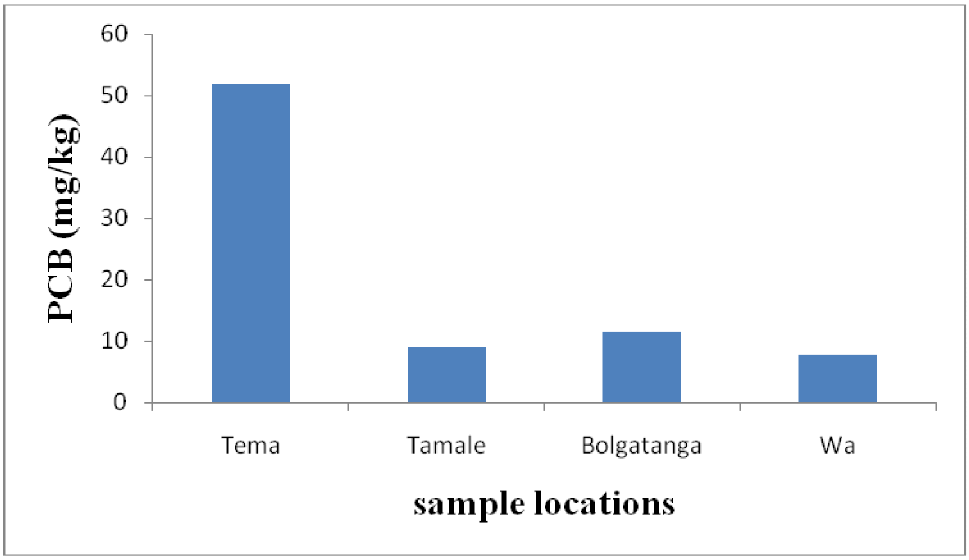


Fig. 4.3: Mean levels of PCBs at different sampling locations

4.6 Variation of PCB levels with soil depth

An interesting trend was observed during the study. Generally, the levels of PCBs in soil samples were found to decrease with increasing depth at all the temporal transformer storage site except Wa and Bolgatanga (Fig. 4.4).

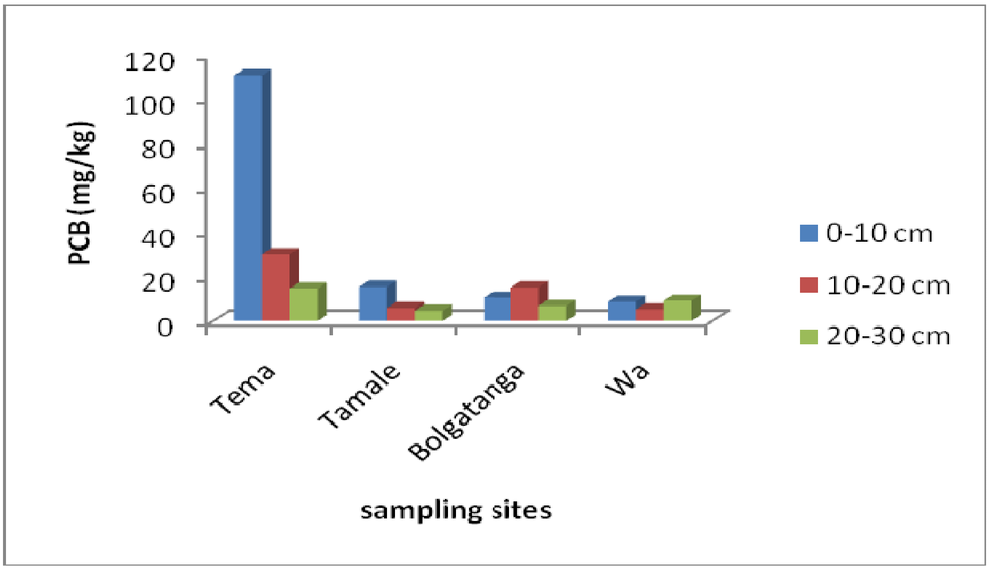


Fig. 4.4: Mean variation of PCB levels with soil depths

At Tema and Tamale, sampling of soil samples was done in the dry season while at Bolgatanga and Wa samples were taken in the wet season. Infiltration of PCBs from the surface of the soil will be very slow in the dry season since there was no moisture to carry it down. Hash weather conditions during the dry season could lead to volatilization of PCBs at the surface of the soil at high temperatures. High solar radiation exposure at various sampling depths could enhance fractionation and evaporation of PCB molecules which might also reduce PCB level. Rains at Wa and Bolgatanga during the sampling period might have led to an increase in PCB levels at 10 – 20 cm and 20 – 30 cm, respectively and caused a deviation from the normal trend. The geology of the area might also be a contributory factor to the levels at different depths. Most part of the three northern regions of Ghana is covered by laterite which does not allow percolation of liquids into the soil easily, hence the slow infiltration rate at the storage sites.

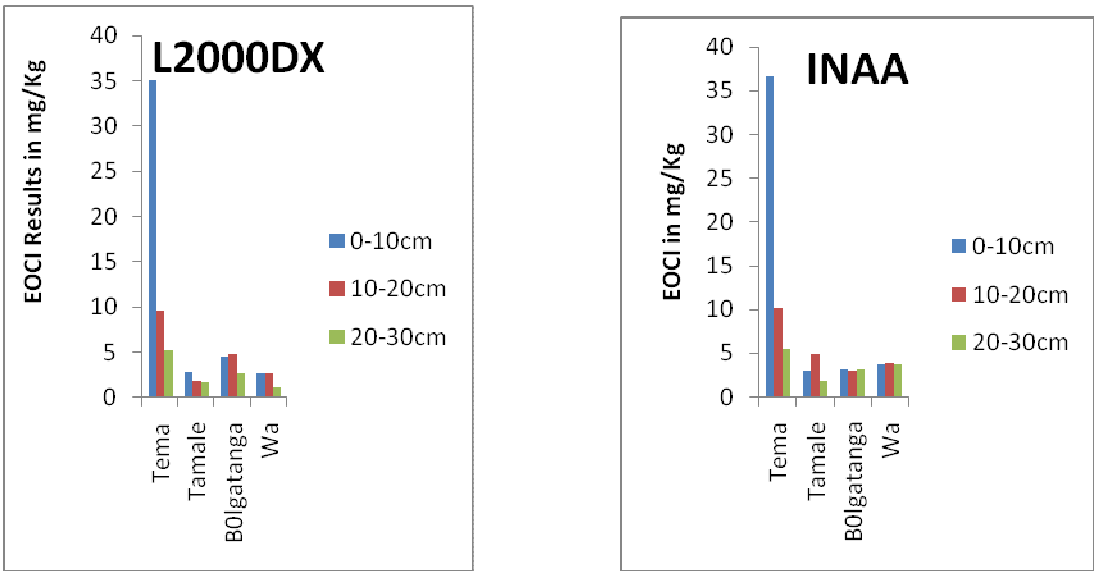
According Ye *et al*. (1992) as pH decreases dechlorination of PCBs occurs and highly chlorinated PCBs congeners in the soils are transformed to less chlorinate by replacing chlorine in biphenyl with hydrogen atom. The pH was found to decrease as depth decreased indicating that as one moves down, the soil becomes more acidic. This implies that dechlorination of PCB will increase with increasing depth hence this could also contribute to the low levels of PCBs with depth. The differences in the PCBs concentration within sampling points with depths could be indication of variability of organic carbon to which chlorine atoms are attached, the ability of the PCB molecule to bind to the surface soils particles and possibility of recent and spatial varying atmospheric deposition. The variability in PCBs concentration with depths could be attributed to different pathways the PCBs molecules might have migrated through before being stranded. Residence time of PCB molecules before dechlorination might also contribute to low concentration of PCBs at that particular depth.

Generally 20 % of soil samples from temporal transformer storage sites analysed had total PCBs concentrations above the 25 mg/kg and 33 mg/kg level recommended by the Canadian Council of Ministers of environment (CCME) and EPA Ghana respectively for the protection of environment and human health and most of them were from the Tema storage site.

4.7 Comparing L2000DX PCB/Chloride Analysis results with Instrumental Neutron Activation

Soil can become contaminated with PCBs through accidents involving the removal and maintenance of transformers and capacitors, through improper disposal or temporary storage of PCB-containing substances. Other synthetic organochlorine compounds such as organochlorine pesticides which are known carcinogens form the major contaminants of concern since they are persistent in the environment. Accurate, fast, cheap and robust method is therefore necessary for the determination of these contaminants in the environment.

The measure of extractable organohalogens such as extractable organochlorine is a way of determining contamination caused by chlorinated organic compounds such as PCBs. Instrumental neutron activation analysis (INAA) and L2000DX PCB/ Chloride Analyser were used to determine the extractable organochlorine (EOCl) in soil samples from the study area. This was to determine the effectiveness of nuclear technology in contaminated site investigation. Fig 4.5 depicts the results obtained using the EPA's L2000DX PCB/ Chloride Analyser and Instrumental Neutron Activation Analysis (INAA) to analyse extractable organochlorine from the soil samples.



(a) (b)

Fig. 4.5: EOCl levels in soil samples using L2000DX PCB/ Chloride Analyser and INAA

Analysis of 50 mg/l L2000 chloride standard using the two techniques gave comparable and favourable results. The L2000DX PCB/ Chloride Analyser registered 48.73 mg/l for the standard while the INAA registered 50.85 mg/l. Soil samples analysed also indicated that the two methods are comparable since there was no significant difference in their results (Appendix 5).

Generally the INAA was found to have recorded higher EOCl values in soil samples than the L2000DX PCB/ Chloride Analyser except at Bolgatanga (Fig. 4.6).

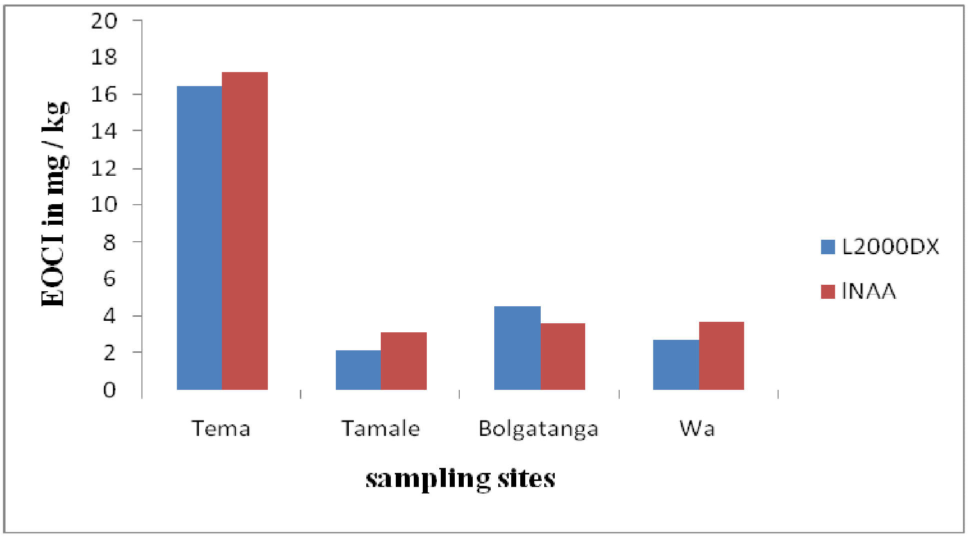


Fig. 4.6: Comparative results of EOCl in soil samples from 0 – 30 cm depth using L2000DX PCB/ Chloride Analyser and INAA

The INAA method has excellent sensitivity and selectivity. This might account for the elevated values recorded by the INAA. The nuclear technique is a fast, highly sensitive and selective technique which analyses both solid and liquid samples without any chemical additions, less sample manipulation and free from reagent and laboratory contamination.

Due to the high sensitivity and accuracy that NAA offers, it is usually used as the referee method when new procedures are being developed (Glascock, 2003). Instrumental neutron activation analysis (INAA) has been classified as the most convenient and the quickest analytical method currently available for simultaneously determination of extractable organochloronated (EOCl), extractable organobrominated (EOBr) and extractable organoiodinated compounds (EOI) in one extract (Diandou Xu *et al*., 2011).

CHAPTER FIVE

Conclusions and Recommendations

5.1 Conclusion

Although PCBs were banned some decades ago their levels were prominently present in our environment.

Analysis of soil samples from four temporal transformer storage sites in Ghana revealed that the soil samples from Tema, Tamale, Bolgatanga and Wa were generally sandy with pH and EC ranging between 6.24 - 7.29 and 44.60 – 188.30 µS/cm respectively. The PCBs levels detected in the soil samples from the various locations varied considerably with mean ranging between 7.69 and 51.92 mg/kg (Fig. 4.2). The highest mean PCB level was recorded at the Tema temporal transformer storage site (51.92 mg/kg) while the least level of 7.69 mg/kg was recorded at Wa storage site. At Tamale the individual levels ranged between 3.57 and 38.70 mg/kg, while at Bolgatanga it was 6.85 – 16.30 mg/kg and Wa 6.08 – 14.70 mg/kg. About 9 % of soil samples from temporal transformer storage sites analysed had total PCB concentrations above the 25 mg/kg and 33 mg/kg level recommended by the Canadian Council of Ministers of environment (CCME) and EPA Ghana respectively, for the protection of environment and human health and most of them were from the Tema storage site. Generally, the levels of PCBs in soil samples were found to decrease with increasing depth at all the temporal transformer storage sites.

Results obtained using the EPA's L2000DX PCB/ Chloride Analyser and Instrumental Neutron Activation Analysis (INAA) to analyse extractable organochlorine from the soil samples indicated that the nuclear technique was a better analytical technique for contaminated site investigation due to its high sensitivity, selectivity, fast and non-destructive nature. The INAA and gamma spectroscopy using HPGe detector coupled with MAESTRO 32 software provided a fast and efficient way to analyse possible PCB contamination in the soil samples and therefore proved to be very reliable method that could be conveniently used for contaminated site investigation.

5.2 Recommendations

Recommendations made from this study are:

(a) The regulatory authorities should ensure that transformers imported into the country are PCB free.

(b) There should be a management system in place at ECG and VRA to track the use and disposal of transformer oils.

(c) EPA, VRA and ECG should team up to track, labelled and properly decommissioned all PCB contained transformers and capacitors in the country.

(d) Transformer storage sites in sensitive locations should be well protected

(e) Since INAA has proved to be sensitive, fast, reliable and efficient in determination of extractable organohalogens, it should be adopted and used as alternative method for contaminated site investigation, especially, with respect to PCBs.

(f) Further studies should be conducted to investigate and assess the impacts of PCBs on humans living in and around these contaminated sites

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Appendix 1: pH of sampled soils

sample ID	Te-1	Te-2	Te-3	Te-4	Te5 Ctrl	Ta1	Ta-2	Ta-3	Ta-4	Ta-5	Ta6 ctrl	Bo – 1	Bo-2	Bo-3	Bo-4	Bo5 ctrl	Wa -1	Wa-2	Wa-3	Wa 4ctrl
0- 10cm	7.29	6.75	6.69	6.88	6.89	6.85	6.48	6.56	6.71	6.85	6.78	6.72	6.64	6.81	6.64	6.89	6.79	6.47	6.97	7.05
10-20cm	6.98	6.68	6.68	6.79	6.54	6.72	6.35	6.51	6.62	6.78	6.59	6.65	6.59	6.76	6.61	6.88	6.44	6.41	6.83	6.98
20-30cm	6.24	6.59	6.56	6.67	6.48	6.66	6.33	6.44	6.6	6.79	6.44	6.58	6.44	6.73	6.61	6.84	6.42	6.40	6.82	6.82

Appendix 2: Electrical conductivity of sampled soil

sample ID	Te-1	Te-2	Te-3	Te-4	Te-5ctrl	Ta-1	Ta-2	Ta-3	Ta-4	Ta-5	Ta-6ctrl	Bo-1	Bo-2	Bo-3	Bo-4	Bo-5 ctrl	Wa-1	Wa-2	Wa-3	Wa-4 ctrl
0-10cm	123	123	119	132	142.2	110.8	166	169	155.4	172.8	143.7	83.4	72.6	128	169	155.3	103	110.2	135.7	128.4
10-20cm	122	119	121	133	151.4	105.7	160	159	148.2	169.6	139.2	135	137.9	133	172	163.7	177	154.9	161.8	144.2
20-30cm	120	120	97.4	45	109.3	107.9	161	166	142.9	177.3	150.3	121	80.1	130	188	176.3	169	143.8	165.4	147.1

Appendix 3: EOCI results obtained from L2000DX PCBs/Chloride in (mg/kg)

sample ID	Te-1	Te-2	Te-3	Te-4	Te-5ctrl	Ta-1	Ta-2	Ta-3	Ta-4	Ta-5	Ta-6ctrl	Bo-1	Bo-2	Bo-3	Bo-4	Bo-5 ctrl	Wa-1	Wa-2	Wa-3	Wa-4 ctrl
0-10cm	3.88	163.00	2.74	3.00	2.41	5.56	1.53	1.93	1.13	4.97	1.92	3.36	NA	4.56	NA	NA	3.48		NA	1.13
10-20cm	4.40	36.00	2.41	2.20	2.81	2.27	1.56	2.06	1.12	1.67	2.26	5.15	NA	4.53	NA	NA	1.94	NA	NA	1.4
20-30cm	2.74	14.40	2.11	1.90	NA	1.99	1.45	1.27	1.14	2.48	2.02	2.75	NA	NA	NA	NA	NA	NA	NA	1.15

Appendix 4: EOCI results obtained from INAA in (mg/kg)

sample ID	Te-1	Te-2	Te-3	Te-4	Te-5ctrl	Ta-1	Ta-2	Ta-3	Ta-4	Ta-5	Ta-6ctrl	Bo-1	Bo-2	Bo-3	Bo-4	Bo-5 ctrl	Wa-1	Wa-2	Wa-3	Wa-4 ctrl
0-10cm	3.74	171.00	3.04	2.40	2.37	5.58	1.53	1.91	1.31	4.95	1.99	3.34	NA	2.7	NA	NA	3.62	3.71	4.61	2.69
10- 20cm	5.13	38.00	2.37	3.00	2.17	12.2	1.39	2.43	1.13	10.6	1.45	2.16	NA	3.8	NA	NA	1.97	4.67	4.83	3.76
20-30cm	2.79	14.90	2.12	2	NA	2.01	1.44	1.31	1.14	2.47	2.03	2.74	NA	3.5	NA	NA	2.89	4.17	4.19	3.49

Appendix 5: Comparative results of EOCl in soil samples using L2000DX PCBs / Chloride Analyser and INAA

EOC (L2000DX)						EOCI (NAA)				
sites code	0-10cm	10-20cm	20-30cm	Min	max	0-10cm	10-20cm	20-30cm	min	Max
Te-1	3.88	4.4	2.74	2.74	4.4	3.74	5.13	2.79	2.79	5.13
Te-2	163	36	14.4	14.4	163	171.41	38.01	14.91	14.91	171.41
Te-3	2.74	2.41	2.11	2.11	2.74	3.04	2.37	2.12	2.12	3.04
Te-4	2.99	2.15	1.92	1.92	2.99	2.39	2.99	1.99	1.99	2.99
Te-5ctrl	2.41	2.81	NA	2.41	2.81	2.37	2.17	NA	2.17	2.37
Mean	35	9.55	5.29	4.72	35.19	36.59	10.13	5.45	4.8	36.99
Ta-1	5.56	2.27	1.99	1.99	5.56	5.58	12.2	2.01	2.01	12.2
Ta-2	1.53	1.56	1.45	1.45	1.56	1.53	1.39	1.44	1.39	1.53
Ta-3	1.93	2.06	1.27	1.27	2.06	1.91	2.43	1.31	1.31	2.43
Ta-4A-C	1.13	1.12	1.14	1.12	1.14	1.31	1.13	1.14	1.13	1.31
Ta-5	4.97	1.67	2.48	1.67	4.97	4.95	10.6	2.47	2.47	10.6
Ta-6ctrl	1.92	2.26	2.02	1.92	2.26	1.99	1.45	2.03	1.45	2.03
Mean	2.84	1.82	1.73	2.13	2.93	2.88	4.87	1.73	1.59	5.02
Bo-1	NA	5.15	2.75	2.75	5.15	3.34	2.16	2.74	2.16	3.34
Bo-2	4.19	NA	NA	NA	NA	NA	NA	NA	4.19	4.83
Bo-3	4.56	4.53	NA	4.53	4.56	2.69	3.76	3.49	2.69	3.76
Bo-4	NA	NA	NA	NA	NA	2.52	3.86	NA	2.52	3.86
Bo-5 ctrl	3.67	NA	4.89	NA	NA	3.67	NA	4.89	3.67	4.89
Mean	4.56	4.84	2.75	2.75	4.84	3.02	2.96	3.12	13.34	4.14
Wa-1	3.48	1.94	NA	1.94	3.48	3.62	1.97	2.89	1.97	3.62
Wa-2	3.63	4.68		3.63	4.68	3.71	4.67	4.17	3.71	4.67
Wa-3	NA	NA	NA	NA	NA	4.61	4.83	4.19	4.19	4.83
Wa-4 ctrl	1.13	1.4	1.15	1.13	1.4	2.69	3.76	3.49	2.69	3.76
Mean	2.75	2.67	1.15	6.9	3.19	3.53	3.81	3.69	10.33	4.22

Appendix 6: Variation of PCBs level with respect to depth

	PCBs(mg/kg) at various depth (L2000DX)					
Sites	0-10cm	10-20cm	20-30cm	Min	Max	PCB range
Te-1	12.2	13.9	8.7	8.7	13.9	8.70-13.90
Te-2	518	114	45	45	518	45.00-518.00
Te-3	7.52	7.66	6.71	6.71	7.66	6.71.00-7.66
Te-4	9.47	6.83	6.09	6.09	9.47	6.09-9-47
Te-5ctrl	6.87	8.9	6.88	6.87	8.9	6.87-8.90
Mean	110.81	30.26	14.68	14.67	110.81	14.67-110.81
Ta-1	38.7	7.21	6.32	6.32	38.7	6.32-38.70
Ta-2	4.42	4.96	5.56	4.42	5.56	4.42-5.56
Ta-3	7.69	6.52	4.03	4.03	7.69	4.03-7.69
Ta-4	3.57	4.41	3.64	3.57	4.41	3.57-4.41
Ta-5	33.8	5.3	7.85	5.3	33.8	5.30-33.80
Ta-6ctrl	4.62	7.15	6.39	4.62	7.15	4.62-7.15
Mean	15.47	5.92	5.63	4.71	16.22	4.71-16.22
Bo-1	6.85	16.3	8.73	6.85	16.3	6.85-16.30
Bo-2	NA	NA	NA	NA	NA	NA
Bo-3	14.4	14.08		14.08	14.4	14.08-14.40
Bo-4				NA	NA	NA
Bo-5 ctrl	NA	NA	NA	NA	NA	NA
Mean	10.625	15.19	8.73	8.73	15.35	8.73-15.35
Wa-1	11	6.08		6.08	11	6.08-11.00
Wa-2	11.4		14.7	11.4	14.7	11.40-14.70
Wa-3	NA	NA	NA	NA	NA	NA
Wa-4 ctrl	3.57	4.41	3.64	3.57	4.41	3.57-4.41
Mean	8.66	5.25	9.17	5.25	9.17	5.25-9.17